

PATENT SPECIFICATION

1,035,566

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Date of Application and filing Complete

Specification: September 18, 1964.

No. 38239/64

Application made in Japan (No. 50990) on September 21, 1963.

Complete Specification Published: July 13, 1966.

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Index at Acceptance:—C3 P (1A, 1C6B, 1C9, 1C14B, 1C16A, 1C16C, 1C18, 1C20B, 1C20D1, 1D1A, 1D1B, 2A, 2C6B, 2C13C, 2C14B, 2C16A, 2C16C, 2C18, 2D1A, 2K8, 4A, 4C6B, 4C13C, 4C14B, 4C16A, 4C16C, 4C20B, 4C20C, 4C20D1, 4C20D3, 4D3B1, 4K10, 7A, 7C6B, 7C13B, 7C13C, 7C14B, 7C16A, 7C16C, 7C18, 7D2A1, 10A, 10C2, 10C5, 10C6B, 10C8B, 10C8C, 10C9, 10C12B, 10C12X, 10C13A, 10C13B, 10C13C, 10C14B, 10C16A, 10C16C, 10C17, 10C18, 10C20B, 10C20C, 10C20D1, 10C20D3, 10D1A, 10D4A, 10FX, 10K4, 10P1D, 10P1E1, 10P1E3, 10P1E4, 10P3, 10P4B, 10P6H, 10T2B); B2 B (4E1A1, 4E1BY, 4E1C1, 4E2D, 4E2Y, 4E3D, 4E4X, 4E6C, 4E7A3, 4E7AY, 4E7B1, 4E7B3, 4E7B4, 4E7B5, 4E8D, 4E8X, 4E9C, 4E9E, 4E9G, 4E9J, 4E9M, 4E9P, 4E9Q2, 4E9Q3, 4E9Q4, 4E9Q5, 4E9Q6, 4E9Q7, 4E9Q8, 4E9QX, 4E9QY); C3 F (2A, 2F, 2H, 3A, 3E, 3G, 3L, 3M, 3R); C4 X11.

Int. Cl.:—C 08 f 29/16 // B44d, C08b, C09k.

COMPLETE SPECIFICATION

NO DRAWINGS

Coating Composition

PATENTS ACT, 1949

SPECIFICATION NO. 1,035,566

In accordance with the Decision of the Superintending Examiner, acting for the Comptroller-General, dated the 3rd day of May 1968, this Specification has been amended under Section 33 in the following manner:—

Page 7, delete line 20, insert

"We are aware of Patent No. 1,018,269 which claims a dispersion comprising 5 to 60% of particles of a fluorocarbon polymer having a molecular weight of 2,000 to 10,000, 40 to 95% of a thermosettable or thermoplastic resin, 0 to 30% of particles of polytetrafluoroethylene having a molecular weight above 500,000 and a solvent for the said resin, the percentages being based on the total weight of polymers and resin solids, a method of forming an adherent low-friction coating on a substrate which comprises applying thereto a dispersion as aforesaid and drying it, at ambient temperature when the said resin is a thermoplastic resin and at an elevated, curing temperature when the said resin is a thermosettable resin, and substrates provided with an adherent, low friction coating by this method, and we make no claim to such a dispersion, method, or substrate. Subject to the foregoing disclaimer, what we claim is:—"

Page 7, delete lines "125, 126 and 127"

THE PATENT OFFICE,
20th June 1968

D 104368/31

SPECIFICATION AMENDED - SEE ATTACHED SHEET

RESERVE COPY
PATENT SPECIFICATION

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Int. Cl.:—C 08 F 29/16 // B44D, C08B, C09K.

COMPLETE SPECIFICATION
NO DRAWINGS

Coating Composition

We, DAIKIN KOGYO KABUSHIKI KAISHA, a Japanese Body Corporate of Shimbankyu Building, 8 Umeda, Kita-ku, Osaka-shi, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to coating compositions. More particularly, the invention pertains to a dispersion containing particles of polytetrafluoroethylene waxes having a molecular weight of from 1,000 to 150,000. Said dispersion is especially useful for providing a surface coating of a high order of lubricant, soil-resistant, parting, water-repellent, oil-repellent, and anti-corrosive properties.

Polytetrafluoroethylene waxes of a low order of molecular weight, such as from 1,000 to 150,000, have a low order of surface free energy and coefficient of friction, and can be easily modified and spreaded out into thin layers or films by the mechanical forces applied thereto. Utilizing such properties, the prior art has applied in a particle state, dispersion or suspension to metals, glass, wood, and the like articles said polytetrafluoroethylene waxes as an agent for forming a lubricant coating on the surface of said articles.

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35 position producing a coating which has

40 To eliminate the aforesaid shortcomings, there has been employed in the prior art a heat treatment process which is applied to the coating at a temperature substantially higher than the melting point of the starting polytetrafluoroethylene waxes. Heat treatment, however, accompanies troublesome procedures, and cannot be applied to the articles having poor heat resistance. The resultant coating, moreover, is not satisfactory in adherence to the substrate.

45 The major object of the present invention is accordingly to provide a polytetrafluoroethylene coating composition which can be dried at a normal atmospheric temperature, producing a protective coating of a high order of durability.

50 Another object of the invention is to provide a polytetrafluoroethylene coating composition producing a coating which has

excellent durability and does not wear off for a long period of time.

A further object of the invention is to provide a polytetrafluoroethylene coating composition producing a coating which has an ability to form thereon a new continuous phase of polytetrafluoroethylene by the action of spreading or melt-flowing caused by the local heating resulting from friction, whereby the durability, particularly the lubricity, of the coating is markedly improved.

A still further object of the invention is to provide a polytetrafluoroethylene coating composition which can be employed as a markedly improved agent for producing onto the substrate surface a coating of a high order of lubricant, soil-resistant, parting, water-repellent, oil-repellent, and anti-corrosive properties.

The above and other objects are accomplished according to the present invention by dispersing particles of polytetrafluoroethylene waxes having a molecular weight of from 1,000 to 150,000 in a high molecular substance-containing solution having an ability to form a film when applied to the substrate surface by dipping, spraying, or brushing, and allowed to dry at a normal atmospheric temperature, namely, without the application of heat treatment to the resultant coating.

The coating thus obtained exhibits a high order of adherence to the substrate surface. The particles of polytetrafluoroethylene waxes employed are uniformly and continuously distributed throughout the surface layer and the intermediate layers of the coating. Said polytetrafluoroethylene particles are further firmly inlaid in the resin layers, so that the particles do not flake away. When the coating is subjected to rubbing or friction, the polytetrafluoroethylene wax particles present in the surface layer of the coating are forced to spread themselves throughout the outermost surface layer of the coating so as to form a continuous phase therein, whereby a high order of protective, lubricant, soil-resistant, parting, water-repellent, oil-repellent, and anti-corrosive effects is obtained. Said continuous phase is also formed when the particles of polytetrafluoroethylene waxes present in the coating is melted by, for instance, repeated friction, and a high order of lubricity is thereby obtained when applied, for instance, to bearings and the like mechanical appliances. Said ability to form a continuous phase, further, is maintained for a long period of time when friction is continued, because a new continuous phase is formed one after another until the coating completely wears off.

The high molecular substance-containing solution employed in this invention includes

all of the solutions having an ability to form a film of the high molecular substance contained therein when dried at a normal atmospheric temperature, namely solutions of high molecular substances, such as cellulose derivatives, polymers of ethylenically unsaturated compounds, and natural and synthetic rubbers. To raise the evaporating ability of the solution, there are employed organic solvents, such as having a specific evaporating rate in the order of from 0.1 to 20.0, preferably from 0.7 to 7.7, in terms of the evaporating velocity of 90 percent n-butyl acetate aqueous solution as 1. When an aerosol propellant is added to the coating compositions of this invention, there can be employed solvents of a lesser degree of evaporating ability.

The high molecular substance-containing solution employed in this invention is prepared by dissolving in an organic solvent a high molecular substance as specified before, and by diluting the resultant solution, where necessary. Desirable solvents and diluents for cellulose ethers, such as methyl cellulose and ethyl cellulose, are ethanol, isopropanol, n-butanol, and the like alcohols; acetone, methyl ethyl ketone and the like ketones; toluene, benzene, and the like aromatic compounds; and ethylene tetrachloride, methylene chloride, carbon tetrachloride, and the like haloalkanes and haloalkenes. Desirable solvents and diluents for cellulose esters, such as nitrocellulose, cellulose acetate, cellulose acetate butyrate, cellulose acetate propionate, cellulose triacetate, and cellulose propionate, are acetone, diacetone alcohol, cyclohexanone, methyl acetate, ethyl lactate, methyl ethyl ketone, dioxane, methylene chloride, nitropropane, chloroform, ethylene dichloride, toluene, xylene, mineral spirits, butanol, and the like. Desirable solvents and diluents for polymers of ethylenically unsaturated compounds such as polyvinyl acetate, polyvinyl chloride, polystyrene, polyacrylic acid esters, vinyl chloride-vinyl acetate copolymer, vinyl acetate-acrylic acid esters copolymer, polymethacrylic acid esters, polyvinyl acetal and polyvinyl butyral, are ethyl acetate, butyl acetate, methanol, ethanol, benzene, cyclohexanone, tetrahydrofuran, toluene, xylene, aniline, chloroform, cresol, phenol, dioxane, ethylene glycol monoethers, and the like. Further, desirable solvents and diluents for rubber-like substances, such as Neoprene, nitrile rubbers and natural rubbers, are toluene, methyl ethyl ketone, methyl isobutyl ketone, ethyl acetate, butyl acetate, and the like. The above specified solvents and diluents are selected in accordance with the species of the high molecular substance to be employed and are used either singly or in combination with each other or one another.

The polytetrafluoroethylene waxes employed in this invention are required to have a molecular weight of from 1,000 to 150,000, particularly from 1,500 to 100,000 for best results. When resinous polytetrafluoroethylene having a molecular weight of more than 150,000 is employed, the particles thereof fail to spread themselves to form a continuous phase in the resultant coating even when rubbing or friction is applied and to produce fluidity due to a high order of melt viscosity even at a temperature higher than the melting point, so that not only the resultant lubricity is not satisfactory but the polytetrafluoroethylene particles distributed in the coating either partially wear off or form agglomerated, elongated lumps, rendering the polytetrafluoroethylene phase more discontinuous and uneven. Such undesirable tendencies are more pronounced with respect to a polytetrafluoroethylene having a molecular weight of more than 1,000,000 and which is placed on the market in the form of suspension under the registered trade mark "Teflon 30" or "Teflon 41X." As compared with the polytetrafluoroethylene waxes employed in this invention, such a substance also displays a higher order of coefficient of friction than the above specified substance and lacks in liquid lubricity due to a high order of melt viscosity, so that the objects of this invention cannot be materialized with those resinous substances as specified above. It is also the case with the polytetrafluoroethylene having a molecular weight of less than 1,000, because the melting point of such substance is low and troublesome procedures should be employed in dispersing such substance in the high molecular substance-containing solution to be employed thereafter.

The polytetrafluoroethylene waxes of a molecular weight of from 1,000 to 150,000 employed in this invention are prepared by a known method, comprising heating a mixture of tetrafluoroethylene and a telogen in the presence or absence of a radical initiator. As a telogen, there is employed in this method one species or a mixture of two or more species of carbon tetrachloride, chloroform, ethylene tetrachloride, trichlorofluoromethane, dichlorodifluoromethane, trichlorofluoromethane, tetrachloroethane, and the like haloalkanes, haloalkenes and halofluoroalkanes. The telogen mixture may also include from 0.5 to 30 percent by weight an aliphatic derivative having a carbon-hydrogen bond, such as isobutane, methyl cyclohexane, liquid paraffin, and the like alkanes and cycloalkanes; dimethyl ether, tetrahydrofuran, ethylene oxide, dioxane, and the like aliphatic ethers; trimethylamine, triethylamine, and the like aliphatic amines; methanol, isopropanol, cyclohexanol, and the like aliphatic alcohols; ethyl mercaptan, dimethyl disulfide, and the like aliphatic sulfur-containing compounds; acetaldehyde, propionaldehyde, and the like aliphatic aldehydes; acetone, methyl ketone, cyclohexane, and the like aliphatic ketones; ethyl acetate, ethyl acetoacetate, and the like aliphatic esters, isolactic acid, and the like aliphatic carboxylic acids; dimethyl phosphite, diethyl phosphite, and the like aliphatic phosphor-containing compounds, dimethyl formamide, and the like aliphatic amides; and dimethyl dichlorosilane, polysiloxane, and the like aliphatic silicon-containing compounds. The radical initiator employed in this method includes benzoyl peroxide, di-tertiary butyl peroxide, azobisisobutyronitrile, diisopropyl peroxydicarbonate, tertiary butyl perbenzoate, and the like organic peroxides and azo compounds.

The polytetrafluoroethylene waxes employed in this invention can also be prepared by other known method comprising pyrolyzing at a temperature above 350°C. a polytetrafluoroethylene resin having a relatively high order of molecular weight in the presence or absence of an alkali metal salt, such as potassium nitrate.

The polytetrafluoroethylene waxes employed in this invention can further be prepared by a method comprising subjecting to ionizing radiation the liquid phase of tetrafluoroethylene in the presence of at least one species of fluoroalkanes as a telogen as specified before. This telomerization reaction proceeds not only at a temperature equivalent to normal atmospheric temperature but under either normal atmospheric pressures or increased or reduced pressures. The reactant fluoroalkane is preferably employed in the order of from 1 to 20 moles on the basis of the starting tetrafluoroethylene as 1 mole. The employment of a fluoroalkane as specified before as a telogen in conjunction with an aliphatic hydrocarbon having a carbon-hydrogen bond or a derivative of said hydrocarbon enhances the ability to control the degree of polymerization, advantageously producing telomers of a molecular weight of 20,000 or less. In this case, said aliphatic hydrocarbon or its derivative is added to the reaction system in the equimolar order or to substantially less molar order than the starting tetrafluoroethylene as 1 mole. Ionizing radiations employed in this process include α -rays, β -rays, γ -rays, X-rays, electron rays, and neutron rays, which are radiated in the order of from 10^4 r/hr to 10^6 r/hr within the range of total radiation of from 10^4 r to 10^6 r. There is used no initiator in this process.

The polytetrafluoroethylene waxes employed in this process.

5 taining 4 percent of dimethylformamide and 0.1 percent of azobisisobutyronitrile in a reaction tower under 15 kg/cm² at 100° C. 3 Parts of the resultant telomer dispersion containing 25 percent of particles of polytetrafluoroethylene waxes having an average molecular weight of 3,000 were added with stirring until homogeneous to 7 parts of a solution consisting of 14 percent of 5 to 7 second nitrocellulose, 14 percent of dammar gum, 4 percent of dibutyl phthalate, 2 percent of cyclohexanone, 1 percent of β -ethoxyethanol, CH₃, CH₂, OCH₂, CH₃, OH, 2 percent of amyl acetate, 20 percent of butyl acetate, 19 percent of ethyl acetate, 6 percent of butanol, 7 percent of methanol, and 11 percent of benzene. The resultant composition was diluted with a mixture of 25 percent of ethyl acetate, 15 percent of butyl acetate, 4 percent of amyl acetate, 5 percent of butanol, 1 percent of β -ethoxyethanol, CH₃, CH₂, OCH₂, CH₃, OH, and 50 percent of benzene, and applied by brushing to the running surfaces of skis, allowing the articles to dry at a room temperature (about 25° C.) for one hour. The resultant milk-white coating imparted a marked running ability to the skis

Example 3

30 20 Parts of the polytetrafluoroethylene dispersion prepared in accordance with Example 2 were blended with 100 parts of a mixture consisting of 5 percent of benzyl cellulose, 22 percent of Manila copal, 7 percent of benzene, 64 percent of methanol, and 2 percent of butylene glycol, and ball-milled for 50 hours until homogeneous. The coatings formed with the resultant composition at a room temperature (about 25° C.) exhibited a marked adherence to the substrate surface of wood, and the coefficient of static friction on glass plates was 0.030.

Example 4

45 20 Parts of the polytetrafluoroethylene dispersion prepared in accordance with Example 2 and containing the particles of polytetrafluoroethylene waxes having an average molecular weight of 8,000 and m.p. 314° C. in the concentration order of 15 percent in carbon tetrachloride were blended until homogeneous with 100 parts of a mixture consisting of 1.43 part of polyvinyl acetate of an average polymerization degree of 300, 2.8 parts of butyl phthalate, 14.3 parts of methanol, 23.6 parts of ethyl acetate, 7.1 parts of butyl acetate, and 42.8 parts of benzene. The resultant composition was applied to rubber rings and dried at a room temperature (about 25° C.) for one hour, forming a coating excelled in slidability for valves.

Example 5

65 30 Parts of the polytetrafluoroethylene dispersion prepared in accordance with

Example 4 were added with stirring until homogeneous to 100 parts of a solution consisting of 10 parts of an 87:13 molar vinyl chloride-vinyl acetate copolymer having an average molecular weight of 100,000 3 parts of dioctylphthalate, 50 parts of benzene, 20 parts of acetone, and 25 parts of ethyl acetate. The resultant composition formed a coating at a room temperature (about 25° C.) exhibiting a marked adherence to the articles treated therewith.

Example 6

10 Parts of the polytetrafluoroethylene dispersion prepared in accordance with Example 4 were blended with stirring until homogeneous with a mixture consisting of 10 parts of polystyrene having an average polymerization degree of 350, 2.5 parts of tricresyl phosphate, and 77.5 parts of benzene. The resultant composition formed a coating at a room temperature (about 25° C.) particularly excelled in water-repellency and in durability at low temperatures.

Example 7

30 Parts of the polytetrafluoroethylene dispersion prepared in accordance with Example 4 were blended with stirring until homogeneous with 100 parts of a mixture consisting of 5 parts of vinyl butyrol resin, 5 parts of 1/2 second nitrocellulose, 7 parts of butyl acetate, 20 parts of ethyl acetate, 44 parts of tricresyl phosphate, 20 parts of ethanol, 31 parts of benzene, 6 parts of butanol, and 2 parts of cyclohexane. The resultant composition formed at a room temperature (about 25° C.) a coating particularly excelled in adherence to metals.

Example 8

50 Parts of polytetrafluoroethylene dispersion prepared in accordance with Example 4 were blended with stirring until homogeneous with 100 parts of a mixture consisting of 3 parts of carbon black, 15 parts of nitrocellulose, 5 parts of dibutyl phthalate, 30 parts of ethyl acetate, 9 parts of butanol, and 15 parts of n-butyl acetate. The resultant composition formed at a room temperature (about 25° C.) a dark coating excelled in lubricity.

Example 9

6.5 Parts of polytetrafluoroethylene wax particles having an average size of 250 microns, an average molecular weight of 2,000, and m.p. 276° C. were admixed with stirring with a solution consisting of 6.5 parts of 5 second R. S. type nitrocellulose, 18 parts of zinc stearate, 3 parts of magnesium carbonate, 2.5 parts of castor oil, 16 parts of ethyl acetate, 6 parts of butyl acetate, and 16 parts of denaturated alcohol, and ball-milled for 24 hours. 100 Parts of the resultant composition were then filled in an aerosol bomb in admixture with 200 parts of a 15:85 (weight ratio)

monofluorotrichloromethane - difluorodichloromethane mixture, and sprayed onto a steel plate, forming at a room temperature (about 25° C.) a coating particularly excellent in parting ability against foamed polyurethane moldings.

Example 10

To a solution consisting of 10 parts of polystyrene having an average polymerization degree of 350, 5 parts of nitrile rubber 2.5 parts of tricresyl phosphate, and 77.5 parts of toluene were added with stirring until homogeneous 10 parts of the polytetrafluoroethylene dispersion prepared in accord with Example 4. The resultant composition produced a coating on a sticking drawer particularly excellent in slidability and other effects as described in Example 1.

20 WHAT WE CLAIM IS:

1. A coating composition comprising a dispersion of the particles of polytetrafluoroethylene wax having a molecular weight of from 1,000 to 150,000 in an organic solvent solution of a high molecular weight polymetric material, said solution having an ability to form a film when dried at a normal atmospheric temperature, and the order of concentration of the total amount of the tetrafluoroethylene wax and the high molecular weight polymetric material present in said polytetrafluoroethylene dispersion being in the order of from 0.1 to 30 percent by weight, of which from 1 to 99 percent by weight is comprised by the particles of the polytetrafluoroethylene wax employed.

2. The coating composition of Claim 1, wherein said polytetrafluoroethylene wax is of a molecular weight of from 1,500 to 100,000.

3. The coating composition of Claim 1, wherein said polytetrafluoroethylene wax is pulverized into particles of a size of less than 100 microns, and then dispersed in said high molecular substance-containing solution.

4. The coating composition of Claim 1, wherein said polytetrafluoroethylene wax is pulverized into particles of a size of from 100 to 500 microns, and then ball-milled in conjunction with said high molecular substance-containing solution.

5. The coating composition of Claim 1, wherein said polytetrafluoroethylene wax is dispersed in an organic dispersing medium, and then dispersed in said high molecular substance-containing solution.

6. The coating composition of Claim 5, wherein said dispersing medium for said polytetrafluoroethylene wax is identical with the solvent medium for said high molecular substance.

7. The coating composition of Claim 5, wherein said dispersing medium for said polytetrafluoroethylene wax is a telogen emulsion.

8. The coating composition of Claim 1, wherein said tetrafluoroethylene particles constitute from 15 to 85 percent by weight of the total solids.

9. The coating composition of Claim 1, wherein said high molecular weight polymetric material comprises at least one of cellulose ether, cellulose ester, polymers of naturally or synthetically unsaturated compounds, or natural or synthetic rubber.

10. The coating composition of Claim 9, wherein said cellulose ether is methylcellulose or ethyl cellulose.

11. The coating composition of Claim 9, wherein said cellulose ester is nitrocellulose, cellulose acetate, cellulose acetate butyrate, cellulose acetate propionate, cellulose triacetate, or cellulose propionate.

12. The coating composition of Claim 9, wherein said vinyl polymer is polyvinyl acetate, polyvinyl chloride, polystyrene, polyacrylic acid esters, vinyl chloride-vinyl acetate copolymer, vinyl acetate-acrylic acid esters copolymer, polymethacrylic acid esters, polyvinyl acetal, or polyvinyl butyral.

13. The coating composition of Claim 9, wherein said rubber is Neoprene, nitrile rubber, chloroprene rubber, or natural rubbers.

14. The coating composition of Claim 1, wherein said high molecular substance-dissolving solvent medium is an organic solvent having a specific evaporating rate of from 0.1 to 20 in terms of the evaporating velocity of 90 percent n-butyl acetate aqueous solution as 1.

15. The coating composition of Claim 1, wherein said high molecular substance-dissolving solvent medium is an organic solvent having a specific evaporating rate of from 0.7 to 7.7 in terms of the evaporating velocity of 90 percent n-butyl acetate aqueous solution as 1.

16. A process for forming a protective coating, comprising treating a substrate surface with the coating composition of Claim 1, and then drying the resultant coating at a normal atmospheric temperature, whereby said polytetrafluoroethylene particles are uniformly and discontinuously distributed throughout the coating formed onto the substrate surface.

17. An article comprising a surface having a protective coating formed by the process of Claim 16.

18. A coating composition substantially as set forth in any one of Examples 1 to 10 herein.

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played in this invention can still further be prepared by a process comprising continuously supplying to a reaction tower a solution consisting of a radical initiator dissolved in a telogen in conjunction with tetrafluoroethylene gas under a pressure of from 1 to 15 kg/cm². During the course of this reaction, there is evacuated from the top of the reaction tower the mixture containing formed telomers, unreacted tetrafluoroethylene, and excess telogen to isolate by condensation the formed telomers in the state of being dispersed in excess telogen from the unreacted tetrafluoroethylene. This continuous process has an advantage of easily controlling the reaction conditions and the distribution of molecular weight of the telomers formed. The reaction proceeds without accompanying any dangerous handling. The telogen and radical initiator employed in this process are identical with those substances employed in the conventional telomerization method as specified before. The above instances as specified hereinbefore, however, are illustrative only and do not necessarily limiting the manufacturing method of the polytetrafluoroethylene waxes employed in this invention.

The coating compositions of this invention desirably contain polytetrafluoroethylene particles as fine as possible. To prepare said compositions, in the first place, the polytetrafluoroethylene waxes prepared in accordance with any of the aforespecified processes are pulverized into particles of a size of less than 100 microns, preferably less than 20 microns, and then dispersed in the high molecular substance-containing solution. In the second place, the particles of said polytetrafluoroethylene waxes having a relatively high order of particle size, such as from 100 to 500 microns, are ball-milled in conjunction with the high molecular substance-containing solution to produce the desired dispersion. In the third place, more desirable effects can be obtained by dispersing the particles of said polytetrafluoroethylene waxes in an organic dispersing medium, and then admixing the resultant dispersion containing polytetrafluoroethylene particles of less than 100 microns with the high molecular substance-containing solution. Said organic dispersing medium includes those organic dispersants which do not allow the solid ingredients to coagulate or precipitate when said polytetrafluoroethylene particles-containing dispersion is admixed with the high molecular substance-containing solution. It is further desirable that said organic dispersing medium is identical with the solvents for the high molecular substance to be employed thereafter. In case the organic dispersing medium which is not identical with the solvent for the high molecular sub-

stance is employed for dispersing the particles of said polytetrafluoroethylene waxes, the amount of the polytetrafluoroethylene dispersion to be admixed with the high molecular substance-containing solution should be limited to such an extent as not to allow the solid ingredients to coagulate or precipitate. The amount of said polytetrafluoroethylene dispersion, however, can be increased when a solvent having a high order of solubility for high molecular substances is employed as a medium for dissolving the high molecular substance to be employed, or when there is added a subsidiary or an auxiliary solvent to the high molecular substance-containing solution. In the fourth place, when the polytetrafluoroethylene waxes to be employed in this invention are manufactured by telomerization, the resultant dispersion which is obtained by separating out the unreacted tetrafluoroethylene and contains in the excess telogen the polytetrafluoroethylene particles of less than 100 microns, is advantageously admixed by itself, namely, without isolating the polytetrafluoroethylene particles from the excess telogen, in the high molecular substance-containing solution. The above specified instances described hereinbefore, however, are illustrative only and not limiting the process for preparing the coating compositions of this invention.

The order of concentration of the coating compositions of this invention varies in accordance with the modes of application, such as dipping, brushing, or spraying. Said coating compositions, however, are usually employed in the order of total solid concentration of from 0.1 to 30 percent by weight, the term 'total solid' being employed to imply the total amount of the polytetrafluoromethylene particles and high molecular weight polymeric material present in the coating composition of this invention. The most desirable effects are obtained when the coating composition of this invention is prepared by confining the total solids present in the composition to the extent of from 20 to 30 percent by weight, and the resultant composition is employed by diluting, where necessary, in accordance with the modes of application as specified before.

The composition ratio of the polytetrafluoroethylene particles present in the coating compositions of this invention ranges from 1 to 99 percent, preferably from 15 to 85 percent for best results, by weight of the total solids present in the coating composition.

There can be added to the coating compositions of this invention a suitable filler and/or diluent. The amount and species of these additives should be carefully determined not to allow the solid contents pre-

sent in the coating composition to coagulate or precipitate. To obtain a specific coloring or matting effect, there may be added in a suitable amount a pigment or a dye, such as chrome yellow, ultramarine, iron oxide, chrome green, aluminum stearate, zinc stearate, calcium carbonate, magnesum silicate, carbon black, barytes, asbestos, silica, titanium white, lake color, and the like. To modify the viscosity of the coating composition and to improve the thickness, adherence, and brittleness of the resultant coating, there may be added in a suitable quantity dammar resin, gum elemi, shellac, denaturated alkylid resin, maleic acid resin, ester gum, phenol resin, urea resin, organic titanate, and the like. Anti-foaming agents, such as octyl alcohol; anti-septic agents, such as pentachlorophenol; and plasticizers can also be added where desirable. The coating compositions of this invention can further be employed in the form of aerosol sprays. In this case, there is added to said composition one or more species of ethane, propane, butane, trichlorofluoromethane, dichlorofluoromethane, and other suitable propellents. The above specified pigments, dyes, plasticizers, denaturants, and other additives can be added to the coating composition at any time throughout the preparing period of said composition. It is, however, desirable to add said additives to the high molecular substance-containing solution during the course of the preparing process thereof.

As stated hereinbefore, the coating compositions of this invention form a durable protective coating onto the substrate surface of the article at normal atmospheric temperatures, a coating which is excellent in lubricant, soil-resistant, parting, water-repellent, oil-repellent, and anti-corrosive capacities. To exemplify the wide range of application of the coating compositions of this invention, there is obtained a marked oilless lubricity when applied to bearings, packings of stuffing boxes, teeth of saws, and other parts of mechanical appliances. When applied to valves, hinges, and screws, there is produced an improved running capacity. When applied to sliding doors, drawers, pulleys, slide rules, fasteners, or chucks, the slidability of the resultant articles is markedly enhanced. When applied to sliding platforms, skis, skates, and the like, there is obtained a markedly improved sliding or running capacity. When applied to wastebaskets, dyeing vats, clotheslines, ropes, wires, sieves, tents, lids, frying pans, baking ovens, bread or chocolate kneaders, there is imparted an effective soil-resistant coating. Lawn mowers, shovels, ploughs, sickles, scythes, rakes, ore containers can be effectively protected from the adhesion of cuttings or muds. When applied to the resin molding devices, the coating compositions of this invention act as an improved parting agent. When applied to the refrigerators, said coating compositions serve as a useful anti-frost agent. Thus, it may be apparent to those who are skilled in the art that the coating compositions of this invention can be applied to almost all sorts of solid articles consisting of wood, metals, plastics, glass, rubber, and the like materials for producing thereon a durable protective coating.

The invention is illustrated in more detail in the following examples, in which all parts and percentages are by weight unless otherwise stated and the viscosity of the nitrocellulose employed is determined in accordance with the standard employed by Hercules Powder Corporation in the United States of America, namely, in terms of the period of time required for the standard steel ball, 5/16 inch (0.797 cm) in diameter and 2.054 grams, to fall plumb down 25.4 cm through a glass tube, 2.54 cm in internal diameter and 36 cm long, containing at 25° C. 100 grams of solution dissolving 12.2 grams of mixture of 20 parts by weight of ethanol, 25 parts by weight of ethyl acetate, and 55 parts by weight of benzene.

Example 1

One part of polytetrafluoroethylene molding scraps having a molecular weight of 1,500,000 was blended with stirring with 5 parts of potassium nitrate at 450° C. for 20 minutes. 9 Parts of the resultant polytetrafluoroethylene waxes having an average particle size of 300 microns, and m.p. 287° C. were added to 100 parts of a solution consisting of 8.7 percent of acetyl cellulose, 2.6 percent of triphenylphosphate, 58 percent of acetone, 10.3 percent of ethyl acetate, 8.4 percent of 1-mitroprene, and 1.7 percent of butanol, and ball-milled for 24 hours until homogeneous. The resultant liquid composition contained particles of polytetrafluoroethylene waxes in the order of about 50 percent in relation to the total solids.

The composition thus prepared was then diluted with a mixture of 4 parts of CH₂Cl₂, OCH₃, CH₃, O, OC, CH₃, and 13 parts of toluene, and applied to the sliding surfaces of a sticking drawer, allowing the articles to dry at a room temperature (about 25° C.) for one hour. The resultant coating imparted to the articles an excellent slidability. No flaking or deterioration took place even after daily use for 6 months.

Example 2

Tetrafluoroethylene was continuously telomerized with carbon tetrachloride con-